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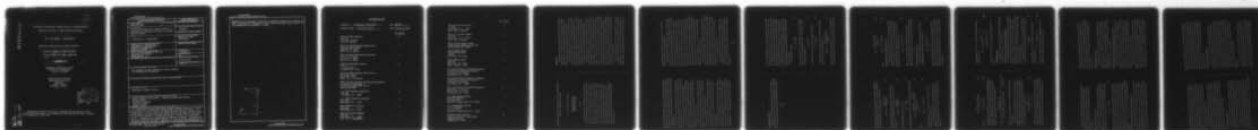   AUG 77   I OREF, B S RABINOVITCH   N00014-75-C-0690
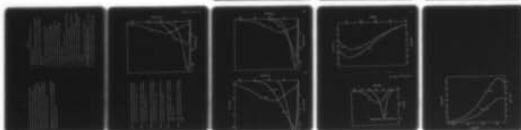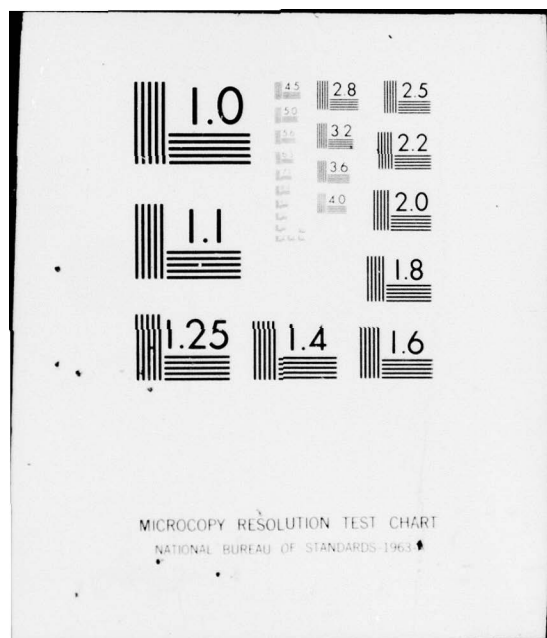UNCLASSIFIED   NR092-549-TR05   NL

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Vibrational-Translational Energy Transfer in Atom-Polyatomic

Molecule Collisions in Thermal Reaction Systems

by I. Oref and B. S. Rabinovitch

27p.

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Vibrational-translational energy transfer probabilities and collisional efficiencies are calculated for atom-polyatomic molecule collisions. It is assumed that a collision complex is formed and that the total internal vibrational energy is statistically distributed among all the modes of the complex. An attractive potential is assumed and account is taken of the centrifugal barrier. Conservation of system angular momentum is imposed. Convolution of the several thermal distribution functions is carried out and completeness and detailed balance are observed. Comparison of calculated quantum statistical

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quantities with experiment is made for the thermal isomerization of methyl and ethyl isocyanide in the presence of heavy atomic bath gases, such as Xe or Ar, and semiquantitative agreement is found.

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Vibrational-Translational Energy Transfer in Atom — Polyatomic Molecule
Collisions in Thermal Reaction Systems[1]

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Abstract

Vibrational-translational energy transfer probabilities and collisional efficiencies are calculated for atom-polyatomic molecule collisions. It is assumed that a collision complex is formed and that the total internal vibrational energy is statistically distributed among all the modes of the complex. An attractive potential is assumed and account is taken of the centrifugal barrier. Conservation of system angular momentum is imposed. Convolution of the several thermal distribution functions is carried out and completeness and detailed balance are observed. Comparison of calculated quantum statistical quantities with experiment is made for the thermal isomerization of methyl and ethyl isocyanide in the presence of heavy atomic bath gases, such as Xe or Ar, and semiquantitative agreement is found.

Introduction

Intermolecular vibrational-translational energy transfer involving poly-atomic molecules is of importance in both reactive and non-reactive gas-phase chemical systems. A few models and methods which treat the details of this process have been developed in recent years and are briefly recalled.

In one theory which has been applied to the results of inelastic scattering in molecular beam experiments,[3-5] it is assumed that the dominating interactions are long range r^{-6} forces and that a collision complex is formed in which available energy is statistically distributed. Decomposition of the complex occurs when the translational energy in the reaction coordinate exceeds the height of the centrifugal barrier. Extension of a statistical model to include rotations has recently been made for atom-molecule exchange.[6]

The inelastic scattering of vibrationally excited KBr by small non-polar partners[4] has been explained by assuming near-colinear impulsive collisions with an anharmonic oscillator; the effect of rotation was not taken explicitly into consideration. In this model, certain collisional configurations were excluded. The effect was to limit the size of the energy step transferred per collision. The theory does not always agree with experiment as ΔE is predicted to be more efficient than Ar, contrary to experimental findings. However, collision of vibrationally excited KBr with polyatomic bath molecules[7,8] could be explained by an extension of Lin and Rabinovitch's model[9] of complex formation with partial participation of vibrational modes of the polyatomic bath molecules. It was found by Fisk, et al.,[7,8] that more than one model was necessary to explain all of their experimental results.

A statistical phase space theory[10] for a bimolecular reaction of a spherical top with spherical top or linear species has been applied to ion-molecule reaction with use of an r^{-4} potential. It was found that the reaction cross section for $C_2H_4^+ + C_2H_4$ agrees only qualitatively with theory inasmuch as the

energy transfer leads to enhancement of energy transfer. A comprehensive review of the subject has been given recently.[18a]

In the quantum statistical model which is developed here, and which uses the potential of refs 1 and 3, collisional energy transfer for thermal systems is calculated for atom - molecule interactions under certain simplifying assumptions. A thermal system in which one of the colliding pair is a polyatomic molecule, with many vibrational-rotational internal modes, is difficult to handle. The internal energy distribution of the molecule must be convoluted with that for relative translational energy. The calculations are carried beyond the computation of energy transfer probability distribution functions. for each given initial condition, to the evaluation of average energy transfer efficiency quantities. Finally, the requirements of completeness and of detailed balance, which are usually omitted in calculations in non-thermal experimental systems, must be adhered to as a very stringent criterion on otherwise discretionary aspects of the calculation. In this circumstance, some simplifying features must be imposed on the calculation.

Not many suitable and reliable experimental systems are known in thermal studies. Application of the model is made to the isocyanide system. Collisional energy transfer probabilities and collisional efficiencies have been calculated for methyl and ethyl isocyanide molecules with Xe bath gas, and results are compared with experiment. The agreement is found to be satisfactory from a qualitative and semi-quantitative point of view. The results help to delineate some details of the energy transfer process.

Since this manuscript was written, a paper has just appeared by Holmlid and Rynefors[18b] who have also imposed the condition of completeness on the model of refs 3,4 and have given a re-interpretation of molecular beam experiments. They used a classical density of states treatment to facilitate their calculations.

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experimental energy dependence of the cross section decreases much faster than predicted by the theory. Better agreement of theory and experiment was obtained for the product kinetic energy distribution; however, improvements in the results in polyatomic systems requires a detailed knowledge of the potential hypersurface at the reaction zone.

Another model[11] for the lifetime distribution of intermediate complexes formed in ion-molecule reactions involves an r^{-4} potential and takes into consideration the centrifugal barrier. No account of the initial internal energy distribution was reported and a stepladder type deactivation was assumed.

Quack and Troe[12] have developed a so-called statistical adiabatic channel model in which a strong complex is formed between a highly interacting atom-diatomic pair. With use of an extrapolation procedure of a Morse potential between molecular complex and the separate product fragments, they obtained the energy distributions of the products.

Another approach which utilized a Morse or truncated harmonic oscillator potential function for atom-diatomic collisions was developed by Johnston and Birks.[13] It was concluded that only levels far below the threshold energy for decomposition contribute significantly to reaction.

Still another treatment for collisional energy transfer has been given by Kohimaier, Nowak and Sire[14] in which the atom-polyatomic molecule interaction is approximated by a Morse interaction potential for an atom and a damped harmonic oscillator.

Several empirical distribution functions have been applied to describe collisional energy transfer probabilities, of which the stepladder and exponential forms are the most commonly used.[15,16] Penner and Forst[17] developed a theory for vibrational-rotational energy transfer in the thermal dissociation of diatomic molecules. The transition probabilities are empirical exponential or gaussian forms. It is found that rotational, in addition to vibrational

Description of the model

Consider a collision between a bath atom and a reactant molecule having translational energy, E, in the center of mass coordinate system. The bath atoms are in excess so that thermal equilibrium is established after each collision.

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If the collision trajectory is such that the impact parameter is below a given value, b_{max}, a short-lived complex is formed. Calculations are made for the case that molecular angular momentum is small relative to system angular momentum. The energy content of the complex (exclusive of its overall rotational energy and of translational energy in the reaction coordinate) is randomized. The complex decomposes with translational energy in the reaction coordinate, ε', different from the energy in the incoming channel. The distribution in E' (= B + ε'), the sum of rotational and translational contributions to total relative translational energy in the outgoing channel (indicated always by a prime), is calculated.

The system potential energy is

$$V(r) = -\frac{C}{R^6} + \frac{J^2}{2\mu r^2} \tag{1}$$

where C is a constant and μ is the reduced mass. The top of the centrifugal barrier is at $r = r_{max}$, corresponding to dV/dr = 0. The rotational energy of the collision complex, B, is

$$B = J^3 (54c\mu^3)^{-\frac{1}{2}} \tag{2}$$

The collision complex has maximum angular momentum corresponding to

$$J_{max} = (54c\mu^3 E^2)^{1/6} \tag{3}$$

The rate coefficient for the dissociation of the complex in the region at r_{max} is given, according to RRKM theory, by

$$k(E_T, B, \epsilon^+) = \frac{f(\epsilon^+) N^+(\epsilon^+) N^+(E_T - B - \epsilon^+)}{N^*(E_T - B)} \tag{4}$$

where, N(E) = density of states at energy E; $E_T = W + E$; ϵ^+ = translational energy in reaction coordinate; W = internal energy of the polyatomic molecule;

and superscripts + and * denote complex and excited molecules, respectively. The product $f(\epsilon^+)N^+(\epsilon^+)$ may be written[16] as 1/h. The total rate coefficient for each E_T and B is given by summing eq. 4 over all possible ϵ^+.

$$k(E_T,B) = \frac{1}{h} \frac{\sum_{\epsilon^+=0}^{E_T-B} N^+(E_T-B-\epsilon^+)}{N^*(E_T-B)}$$ (5)

The probability of the separating pair having translational energy E'. $P(E_T,E')$. is calculated under the assumption B = B'. Then E' = B + ϵ^+. and $P(E_T,B)$ is

$$P(E_T,B) = \frac{k(E_T,B,\epsilon^+) P(B)}{k(E_T,B)}$$ (6)

where the probability of a given B, P(B), is

$$P(B) = 2JdJ/J_{max}^2 .$$ (7)

Incorporating eqs. 2-5 and 7 into 6 yields the quantum statistical expression.

$$P(E_T,B) = \frac{N^+(E_T-B-\epsilon^+)}{\sum_{\epsilon^+=0}^{E_T-B} N^+(E_T-B-\epsilon^+)} \frac{2}{3} \left(\frac{B}{E}\right)^{2/3} \frac{dB}{B} .$$ (8)

and

$$P(E_T,E') = \sum_{ij} P_{ij}(E_T,B) ;$$ (9)

the summation runs over all j values of B and i values of ϵ^+ for all combinations such that $B_j + \epsilon_i^+ = E'$.

For a thermal system, averages of the thermal distributions must be evaluated. The average of $P(E_T,E')$ must be taken over all values of the incoming translational energy, in the center of mass coordinate system, and is given by

$$P(W,E') = \frac{\int_0^\infty P(E_T,E') P(E) dE}{\int_0^\infty P(W,E') dE'} .$$ (10)

where $$P(E)dE = E e^{-E/RT} dE/(RT)^2$$ (11)

Calculation of Energy Transfer Probabilities

The outcome of an energy transfer event is evaluated by comparing the input probability P(E) with the output P(W,E') such that for any ΔE (where ΔE = E'-E), activation occurs when P(E) > P(W,E') at the same energy, and deactivation occurs when the reverse relation holds. The probability of obtaining a given ΔE for all combinations of E and E' is

$$P(W,\Delta E) = \sum_i P(W,E') \cdot P(E) ;$$ (12)

where i is a running index over all combinations of E' and E, i.e., E_j' and E_k, such that $\Delta E = E_j'-E_k$; $P(W,\Delta E)$ is properly normalized by the conservation relation, $\int_{-\infty}^\infty P(W,\Delta E)d\Delta E = 1$, and transitions with ΔE = 0 are included.

The Fraction of Molecules above E_o

The fraction of molecules at each W which after collision are above the threshold energy for decomposition can be found by

$$Q(W) = \int_{E_o-W}^\infty P(W,\Delta E) d(\Delta E)$$ (13)

Equation 13 is weighted by the internal energy population and integrated over all internal energies to yield the total number of molecules with energy above E_o which, in the low pressure limit of a thermal reaction, is proportional to the rate coefficient for decomposition. The collisional efficiency is then defined as:

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$$B = \int_0^{E_0} Q(W)B_{ss}(W)dW \bigg/ \int_{E_0}^{\infty} B(W)dW \qquad (14)$$

where,
$$B(W) = N(W) e^{-W/RT} \qquad (15)$$

and the integral in the denominator is simply the strong collision expression divided by ω. $B_{ss}(W)$ is the steady state population which differs from the equilibrium population because of the depletion of levels below E_0 due to reaction. $B_{ss}(W)$ may be found[13] by iteration of the expression

$$B_{ss}(W_i) = \frac{\int_0^{E_0} P(W_j,\Delta W)B(W_j)\delta' dW_j}{\int_0^{E_0} P(W_i,\Delta E)\delta' d(\Delta E) - \int_0^{E_0} Q(W_i)B(W_i)dW + Q(W_i)} \quad ; \delta' = 0, \text{ for } j = i; \quad (16)$$
$$= 1, \text{ for } j \neq i;$$

where $\Delta W = |W_j - W_i|$, and subscripts j and i signify different states of the internal energy.

Exploitation of the above relations is subject to economic realities. To obtain $P(E_i,E')$ for each allowed combination of W, E, B, ϵ^+, mentioned before, far exceeded our computational resources and some judicious approximations had to be made. We have taken the approach which was suggested in ref. 1 and used the integral form of $P(B)$ to obtain

$$P(B) = \left(\frac{E'}{E}\right)^{2/3} , \text{ for } E' < E ;$$
$$= 1 \qquad , \text{ for } E' > 1: \qquad (17)$$

Implicit in this approach is, of course, the fact that the number of states in the denominator of eq. 8 is assumed to be independent of B. To abide by the physics of the system, detailed balance was checked independently and made to agree by introducing a correction function for the approximation which is

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introduced by the use of eq. 17. The final expression, which was used instead of eq. 9, is

$$P(E_T,E') = N(E_T-E')\left(\frac{E'}{E}\right)^{2/3} \quad ; E' < E$$
$$= N(E_T-E') (E'-E)^{\alpha} \quad ; E' > E \qquad (18)$$

The value of α was determined by the required detailed balance of the system.

Results and Discussion

As examples, we consider the thermal isomerization of CH_3NC and C_2H_5NC, with heavy atoms such as Ar or Xe as bath molecules. The thermal population distribution of CH_3NC and C_2H_5NC.

At low and moderate temperatures, the equilibrium population distribution function $B(E)$ for C_2H_5NC, and especially for CH_3NC, is discrete at the low energy end. This behavior of polyatomic molecules is unimportant if the energy region of interest is close to the value of E_0. However, if collisions with large ΔE are important,[13,17,19] the quantum effect will appear as fluctuations in the function $P(W,\Delta E)$.

The normalized distribution function $B(E)$ was independently checked by comparing the average thermal energy $<E>$ computed from eq 19, evaluated by

$$<E> = \int_0^{\infty} EB(W)dW \qquad (19)$$

numerical integration, with the value obtained from the statistical — thermodynamic relation,

$$<E> = - R\, d(\ln Q_v)/d(T^{-1}) \qquad (20)$$

where Q_v is the vibration partition function. Agreement within 10% was required and was obtained by varying the grain size of W.

The steady state populations were evaluated from eq. 16 and were used to find B in eq. 14. It was found that there is a modest (from a few percent up to 10-15%) depletion of the populations in the levels just below E_0; these levels are still the major contributors to reaction, as discussed later.

Detailed balance and the value of α

The present model uses the parameter, α (eq. 18), in the probability function $P(W,E')$. It was introduced to account for the fact that the integral over all values of B (eq. 9) is replaced by an approximate expression. An independent check of the appropriate value of α is given by detailed balance,

$$B(E_j)P_{ji} = B(E_i)P_{ij} \qquad (21)$$

It was required that detailed balance should be obeyed to within an average of 10% over the whole interesting range of energies. This stringent requirement on the value of α is an additional condition usually not imposed in the treatment of non-thermal systems. (If α were treated merely as an adjustable parameter, _exact_ concordance between theory and experiment could be obtained.) The values of α used are 1.30 ± 0.05 and 1.20 ± 0.05 for CH_3NC at 550°K and 850°K, respectively, and 1.20 ± 0.05 and 1.00 ± 0.05 for C_2H_5NC at 550°K and 850°K, respectively.

Translational energy distribution in the outgoing channel.

Sample curves for the translational energy distribution in the exit channel are given in Figures 1-3. For comparison, the thermal translational energy in the incoming channel is shown as well. The value of α used at each temperature was chosen independently to give the best agreement with detailed balance. The "cooling" effect of collisions can be seen clearly when the higher energy curve at 38 kcal mole^{-1} internal energy is compared with the one at 9.2 kcal mole^{-1}.

The former has a large high energy tail because the leaving atom carries with it a relatively larger amount of translational kinetic energy than for the case of collision with a low internal energy polyatomic molecule. Large values of ΔE are not completely negligible for collisions of an atom with high internal energy molecules. This is a consequence of a mechanism in which statistical distribution prevails.

Collision probabilities $P(W,\Delta E)$

Two illustrations of the collision probability function $P(W,\Delta E)$ are given in Figure 4 for two cases: a low internal energy case (9.2 kcal mole^{-1}) and a high internal energy case (38 kcal mole^{-1}). The shapes of the curves vary with the energy content of the molecule, from almost symmetric for the low case to the skewed high energy one. The collision probability for the removal of large ΔE is larger, the higher the internal energy.

Fraction of molecules at each energy brought above E_0 by collision.

The total fraction of molecules which decompose at the low pressure limit is the sum of the fraction of molecules, at each internal energy, which are transported to energies above E_0, as given by $Q(W)$(eq. 13). For the isocyanides. E_0 is 38 kcal mole^{-1}. Figure 5 refers to CH_3NC and Figure 6 to C_2H_5NC. It can be seen that there is some contribution to reaction from levels which are far below E_0. The extent of the contribution depends on the reacting molecules and the temperature at which the reaction is taking place.

The collision probabilities which were calculated in this work are intermediate in character between models which are used currently[15] or were developed before for simple atom-diatomic dissociation systems.[13,17,19] An example of the latter case is the work of Johnston and Birks[13] who considered three models for energy transfer: ladder climbing with a truncated harmonic oscillator, and truncated and Morse oscillators with all transitions allowed. Their conclusion was

that a truncated harmonic oscillator model with all transitions allowed provides the best agreement with the experimental results; only levels far below E_o were found to contribute significantly to reaction. According to their model, the populations of levels just below E_o are completely depleted and do not contribute to steady state reaction. Similar arguments were put forward by Kiefer, et al.[19] Penner and Forst[17] maintained that the depletion of the higher state is due not to the probability of vibrational energy transfer but to the effect of rotational energy transfer.

As mentioned earlier, popular mathematical expressions in use for collisional transfer probabilities are the empirical step-ladder and exponential models. As is clear from Figures 5,6, in the present model there is really no single group of levels which contribute to reaction; there is a distribution of ΔE values which is a function of the temperature and the individual molecule-atom pair which are involved in the collision process. The present results can be considered as intermediate between the two cases.

The collisional efficiency, β

As an independent check of the calculations, the average β was calculated for each collision pair: for C_2H_5NC, β = 0.92 ± 0.05 at 550°K, as compared with the experimental value[20] 0.39-0.44 for Ar and Xe at 504°K; for CH_3NC, β = 0.84 ± 0.05 at the same temperature, compared to the experimental results[8] 0.31-0.25.

If the density of states were the only factor which entered into the collisional efficiency, one would expect $\beta_{CH_3NC} > \beta_{C_2H_5NC}$; CH_3NC has fewer degrees of freedom than C_2H_5NC and therefore the average energy per oscillator is larger and leads to higher probabilities for decomposition of the collision complex. That the experimental and calculational results agree, i.e., that $\beta_{CH_3NC} < \beta_{C_2H_5NC}$,[17]

suggests that in this model the "small" molecule behavior of CH_3NC may affect the results of energy transfer through the value of α in eq. 18, which in turn influences the collisional probabilities. Moreover, the simplifying assumption regarding conservation of angular momentum cannot be supported in general. One source of the difference between the efficiencies calculated here and the lower values calculated by Lin and Rabinovitch[21] is the fact that a semi-empirical cut-off in the maximum amount of energy transferred to the reaction coordinate was applied by the latter authors. The cut-off was introduced as a restriction on a purely statistical model.

Dependence of β on the temperature

With increase of temperature, the substrate population shifts to higher energies; $P(W,E')$ has a larger high energy tail and the incoming translational energy distribution also shifts to higher energy (see Figure 2) to an extent that makes deactivation less probable at energies below E_o. As a result, the value of β decreases with increase in temperature — from values of β = 0.84 and 0.92 at 550°K to values of β = 0.66 and 0.70 at 850°K, for CH_3NC and C_2H_5NC, respectively. Very little quantitative or qualitative information on the temperature dependence of β in any thermal system is available. For the isocyanides, a decrease in β from 0.29 to 0.21 was measured[22] over the range from 483°K to 600°K in the CH_3NC-He system so that the ratios are in semi-quantitative agreement with the calculation.

Conclusions

A model for energy transfer is presented which essentially contains no adjustable parameters. All probability functions were evaluated quantum statistically; completeness and detailed balance are adhered to strictly. It is found that collisional efficiencies, β, agree qualitatively and semi-quantitatively, in size and in trend, with experimental values in the CH_3NC-C_2H_5NC systems and with the effect of temperature increases; it is found that small

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energy jumps are more important than large ones, as in the exponential or poisson models, but the latter cannot be neglected altogether.

This is the general form expected for energy transfer by weak/atomic bath colliders.[18] The relative contribution to reaction from each initial energy level depends on the specifics of the colliding pair and the temperature. The higher the temperature, the less important is the contribution to reaction of the low-lying vibration states. A population depletion of levels below E_o is found but their relative contribution is still high.

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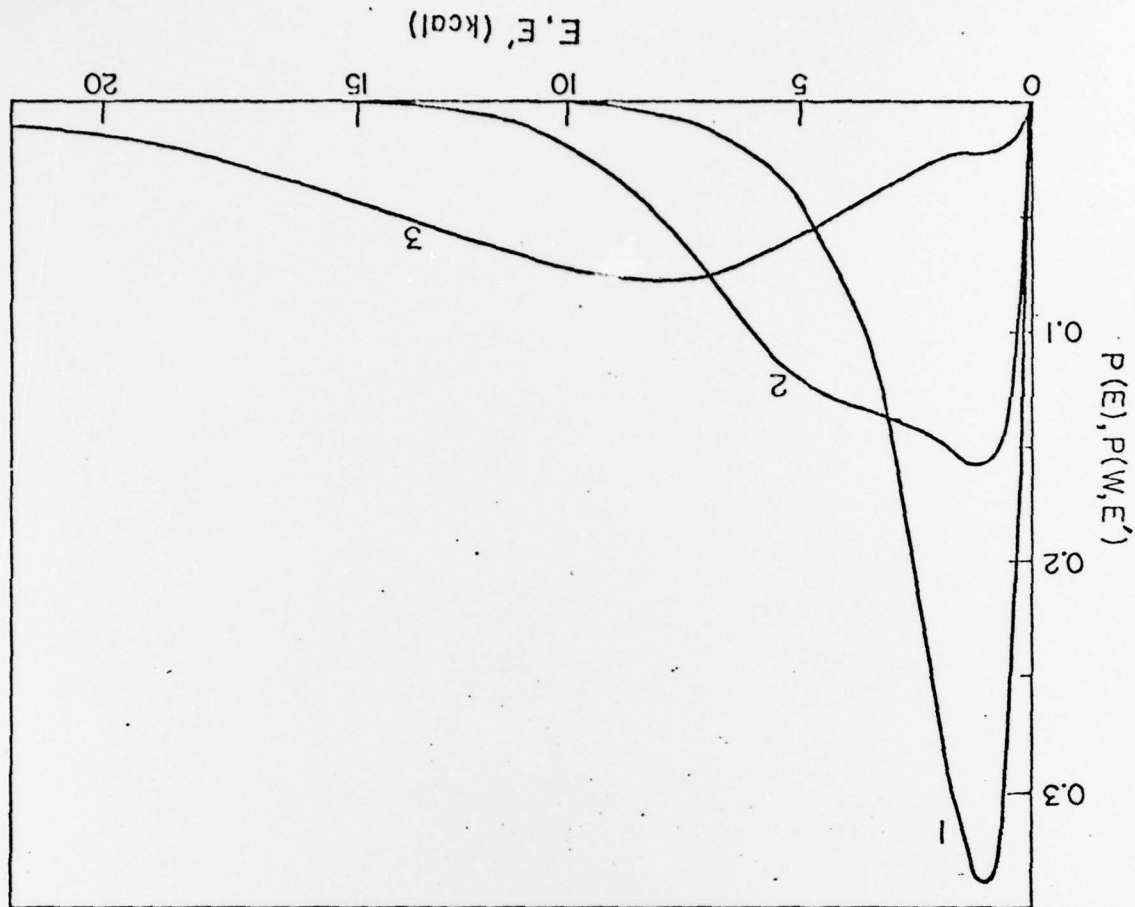21. S. C. Chan, J. T. Bryant and B. S. Rabinovitch, J. Phys. Chem., 74, 2055 (1970).

E,E' (kcal)

P(E), P(W,E')

Figure 1. CH$_3$NC molecule at 550°K: 1) Thermal translational distribution in center of mass coordinate system; 2) P(W,E') at W = 9.2 kcal mole^{-1}, α = 1.3; 3) P(W,E') at W = 38 kcal mole^{-1}, α = 1.3.

Figure 2. CH$_3$NC molecule at 850°K: 1) Thermal translational distribution in center of mass coordinate system; 2) P(W,E') at 9.2 kcal mole^{-1}, α = 1.2; 3) P(W,E') at 38 kcal mole^{-1}, α = 1.2.

Figure 3. C$_2$H$_5$NC molecule at 550°K: 1) Thermal translational distribution in center of mass coordinate system; 2) P(W,E') at 9.2 kcal mole^{-1}, α = 1.2; 3) P(W,E') at 38 kcal mole^{-1}, α = 1.2.

Figure 4. Energy transfer probabilities P(W,ΔE) for C$_2$H$_5$NC at 550 and α = 1.2: 1) W = 9.2 kcal mole^{-1}; 2) W = 38 kcal mole^{-1}.

Figure 5. Fraction of CH$_3$NC molecules of above E$_0$, Q(W), for a given internal energy W: 1) left hand scale, T = 850°K, α = 1.2; 2) right hand scale, T = 550°K, α = 1.2.

Figure 6. Fraction of C$_2$H$_5$NC molecules above E$_0$, Q(W), for a given internal energy W: 1) right hand scale, T = 550°K, α = 1.2; 2) T = 850°K, α = 1.0.

fig 5

fig 4

W (kcal)

35   30   25   20   15

Q(W) × 10¹²

$Q(W) \times 10^{12}$

$Q(W) \times 10^{7}$

2

1

2   4   9   8   10   12   14

1   2   3   4   5   6   7

Fig 4 typical Maxwell

ΔE (kcal)

20   15   10   5   0   -5   -10

P(W, ΔE)

0.1

0.2

2

1

deactivation ← → activation